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Abstract

The dynamic behavior of a dense hard-sphere liquid is studied by numerically integrating a set of Langevin equations which incorporate a free-energy functional of the Ramakrishnan-Yussouff form. Several interesting features of glassy dynamics, such as stretched exponential decay of correlations, two-stage relaxation and Vogel-Fulcher growth of relaxation times, are reproduced and new results on the wavenumber dependence of the kinetics are obtained.

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The present understanding of the slow non-exponential dynamics of dense liquids near the glass transition is far from complete and there is an obvious need for the development of analytic and numerical methods to address various aspects of this problem. In this letter, we describe a study of the dynamic behavior of a dense hard-sphere liquid which is based on a method not previously used for this system: direct numerical integration of a set of Langevin equations which describe the nonlinear fluctuating hydrodynamics (NFH) [1] of the system. Information about the equilibrium structure of the liquid is incorporated in the Langevin equations via a free-energy functional of the Ramakrishnan-Yussouff (RY) form [2] . It has been shown recently [3] that this free energy functional provides a correct mean-field description of the glass transition in this system in terms of the development of a large number of 'glassy' local minima of the free energy as the density is increased beyond the value at which equilibrium crystallization occurs. Our study is motivated by a number of important considerations. By comparing the results of our calculation with existing molecular dynamics data [4] , we are able to test the validity of the 'mesoscopic' NFH description which uses coarse-grained number and current density variables instead of the coordinates and momenta of individual particles. Since the mode coupling (MC) description of the kinetics of dense fluids [5] can be derived from a perturbative treatment of the NFH equations we consider, our calculation, being essentially non-perturbative in nature, provides a test of the validity of the approximations made in the MC approach. Further, by monitoring which local minima of the free energy are visited during the time evolution of the system, we are able to determine whether the observed dynamic behavior arises from nonlinear couplings of density fluctuations in the liquid or from transitions between different glassy minima of the free energy. The efficiency of the coarse-grained Langevin dynamics enables us to obtain fully equilibrated dynamic correlations over long

time scales.

In our study, we have concentrated on the wavevector and time dependence of equilibrium dynamic density correlation functions, as defined below. We have studied reduced the densities ($n^* = n_0\sigma^3$, where n_0 is the average number density and σ is the hard sphere diameter)$n^* = 0.5$ and the range 0.75 - 0.90 at 0.05 intervals, and wavevectors q well-removed from the upper and lower cutoffs arising respectively from the spatial discretization scale and the sample size. It was found in a recent study [3] that the discretized RY free energy of the hard-sphere system exhibits a crystallization transition near $n^* = 0.83$. Thus, for a part of the density range covered in the present study, the system is in the 'supercooled' state. The slowest characteristic time t^* at constant density, which occurs for wavevectors close to that of the main peak in the static structure factor, has a strong density dependence which is well-described by a Vogel-Fulcher form [6] with parameters very close to those obtained from a similar fit to molecular dynamics data [4]. This result establishes the validity of the NFH description and also points out the importance of incorporating detailed information about the liquid structure in the NFH equation because a Vogel-Fulcher growth of relaxation times was not observed in an earlier study along similar lines [7] which treated the liquid structure in an approximate way.

We now proceed to describe our calculation. The derivation of the Langevin equations we use is similar to that in Ref.(7). Details will be given in a lengthier work [8] .The NFH equations we consider are:

$$\frac{\partial \rho}{\partial t} + (1/\rho_0)\nabla.(\rho \mathbf{j}) = 0 \qquad (1)$$

and:

$$\frac{\partial g_i}{\partial t} = -(1/m_0)\rho\nabla_i\frac{\delta F}{\delta \rho} - (1/\rho_0)\sum_j \nabla_j(g_i g_j) - (1/\rho_0)\sum_j g_j\nabla_i g_j + (1/\rho_0)\eta\nabla^2 g_i + \Theta_i \quad (2)$$

In these equations, $\rho(\mathbf{r},t)$ and $\mathbf{j}(\mathbf{r},t)$ are the number and current density fields, m_0 is the particle mass, η is the 'bare' shear viscosity and F is a free-energy functional of the RY form:

$$F[\rho(\mathbf{r})] = F_l(\rho_0) + k_B T[\int d\mathbf{r}[\rho(\mathbf{r})ln(\rho(\mathbf{r})/\rho_0) - (\rho(\mathbf{r}) - \rho_0)]$$

$$- 1/2 \int d\mathbf{r} \int d\mathbf{r}' C(|\mathbf{r} - \mathbf{r}'|)[\rho(\mathbf{r}) - \rho_0][\rho(\mathbf{r}') - \rho_0]] \qquad (3)$$

In Eq. (3), F_l is the free energy of the uniform liquid with density ρ_0 and $C(|\mathbf{r} - \mathbf{r}'|)$ is the Ornstein-Zernike direct pair correlation function [9] for which we use the Percus-Yevick form [9] appropriate for a hard-sphere liquid. The random Gaussian noise fields $\Theta_i(\mathbf{r},t)$ obey the statistics[10] :

$$< \Theta_i(\mathbf{r},t)\Theta_j(\mathbf{r}',t') >= -2k_B T\eta\lambda\delta_{i,j}\nabla^2\delta(\mathbf{r} - \mathbf{r}')\delta(t - t'). \qquad (4)$$

Equations (1) and (2) are slightly different from the ones considered in Ref. (7). The differences arise because in the derivation of these equations we have assumed that the total kinetic energy of the system is given by $(m_0/2)\int d\mathbf{r}[|\mathbf{j}(\mathbf{r})|^2/\rho_0]$ while in Ref. (7) the ρ_0 in the denominator was replaced by $\rho(\mathbf{r})$. If that expression for the kinetic energy is used, functional integration of the variables $\mathbf{j}(\mathbf{r})$ produces a $ln[\rho(\mathbf{r})]$ term in the free energy which already appears in Eq. (3).

In our numerical treatment of these equations, we discretize space by dividing the sample volume into cubic cells of dimension $h < \sigma$, taking σ/h incommensurate with N. The numerical methods used to solve the equations of motion are essentially the same as were used in Ref.(7). We use a cubic lattice of size N^3. The results reported here are for $N = 15$ and have been spot checked for size effects by comparing with data at $N = 25$. The integral involving $C(r)$ which must be performed at every time step, is handled by tabulating this function at the beginning of the computation. Details on these and other

computational considerations will be given in Ref.(8). We choose $l_0 = h$ as the unit of length, m_0 as the unit of mass, and $t_0 = l_0/c$, where c is the speed of sound, as the unit of time [11] We also define dimensionless fields $n(\mathbf{r}, t)$ and $\mathbf{j}(\mathbf{r}, t)$. All quantities mentioned from now on should be understood to be in these units. The speed of sound is calculated in terms of the compressibility derived from the Percus-Yevick $C(r)$ and we use a standard formula from kinetic theory [12] for η. The noise variables Θ_i used in our numerical calculations satisfy Eq. (4). As explained in Ref.(7) the factor of λ merely sets the overall scale of the gaussian fluctuations. The precise value of λ is unimportant but it clearly must be small since the density must always be positive. In our calculations, we have used the value $\lambda = 0.001$. In the equations of motion written in terms of dimensionless quantities, all factors of the temperature T drop out as expected and all the coefficients are determined as functions of n^*.

We will focus our analysis on the normalized quantity $C(q,t)$ defined as $C(q,t) = S(q,t)/S(q,0)$ [13] where $S(q,t)$ is the spherical average of the dimensionless dynamic structure factor $S(\mathbf{q},t)$:

$$S(\mathbf{q},t) = \int d^3r e^{i\mathbf{q}(\mathbf{r}-\mathbf{r}')} < \delta n(\mathbf{r},0)\delta n(\mathbf{r}',t) > \qquad (5)$$

where δn denotes the fluctuation of the field n from its average. The angular average is performed over values of $\mathbf{q}$ in the first Brillouin zone in a shell of radius $\pi n_q/N$ and thickness π/N as explained in Ref.(7). We specify q by the value of n_q. Data are collected with particular care to ensure that averages computed are true equilibrium averages, that is, we verify ergodicity in the time scales of concern here. After some transient, which is largely determined by otherwise unimportant initial conditions, we collect at a large number of periodic time bins the products $\delta n(\mathbf{r}, t_0)\delta n(\mathbf{r}', t_0 + t)$. Averaging over a number of time bins n_b covering a time range $t_R = \Delta t n_b$ where Δt is the interval between time bins,

allows us to monitor $S(q,t,t_0)$, the spherically averaged Fourier transform of the collected quantity. For $S(q,t,t_0)$ to be an adequate approximation to the statistical average $S(q,t)$ it is necessary that it be independent of t_0 (no transient dependence) and also of t_R (ergodicity). We find that the time t_0 measured from the beginning of the computational run, must be much longer than the time t_k at which the static current correlations (which we also monitor) reach their equilibrium value given by the equipartition theorem. In fact, both t_0 and t_R must be of the order of several times t^*, the characteristic decay time in the system as defined below, in order for the averages to stabilize. In addition to this, a large number of bins is required for statistically reliable results. The averaged results presented here correspond to a combined total of between 600 and 1750 bins, depending on the density. This is a very large number which produces data of very high statistical quality. We have also checked that the results obtained for $S(q,t=0)$ are consistent with those calculated from purely static considerations. Details on this and on the data collection procedure will be found in Ref.(8).

We now discuss our main results. We have analyzed our data for $C(q,t)$ in the range $6 < n_q < 15$. Our main conclusion is that all of the data can be fitted to the general form:

$$C(q,t) = (1-f)e^{-(t/\tau)^\beta} + fe^{-(t/\tau')} \tag{6}$$

where it is understood that all parameters are functions of n^* and q. This form is quite versatile: in general it represents two successsive exponential decays the first of which is stretched [14] ($\beta < 1$). When τ' is beyond the range studied, it represents a decay to a 'quasinonergodic' regime. If the two time scales are well separated, one has in the region $\tau \ll t \ll \tau'$ a power law decay. If $\tau \approx \tau'$ then Eq.(6) reduces to a single stretched exponential decay. We find that this simpler case is all that occurs at the lowest

densities, for all wavevectors. As the density increases, the behavior changes, first in the q region where the static $S(q)$ has its second peak, which in our units this corresponds to $11 < n_q < 15$. At the highest density some indications of the onset of this behavior are seen at the q value of the main peak of $S(q)$ near $n_q = 8$. For these values of q we find, within the density range studied, that the ratio τ'/τ increases very sharply with density, reaching values larger than ten at $n^* = 0.9$. The quantity f, while depending on q, is a slowly varying function of n^*. This is in agreement with a MC prediction.[5] In some cases the time τ' is beyond the time region studied, particularly when f is small. A sample of our results, with best fits to the above form, is given in Figs 1 and 2. We observe, at higher densities and smaller wavelengths, either two successive decay regimes or a decay to a small finite value f from which presumably the system decays to zero at later times.

The time τ is a very strong function of wavevector, with a sharp maximum at the value of q where $S(q)$ has its main peak. (At the peak the decay is still single-mode). We identify this value of τ with the characteristic time of the slowest mode in the system, t^*. We plot this quantity in Fig.(3) as a function of $1/n^*$. As shown in the Figure, we find an excellent fit to the Vogel-Fulcher [6] law:

$$t^*(n^*) = \alpha e^{\gamma/(v-v_c)} \tag{7}$$

(where $v \equiv 1/n^*$) with the critical value of v_c corresponding to $n_c^* = 1.20$. This is in excellent agreement with the Monte Carlo result of Ref. (4) where $n_c^* = 1.21$ was obtained.

It is instructive to briefly discuss these results in connection with mode coupling theory (MC), Monte Carlo molecular dynamics (MD) simulations and experiment. A fuller presentation will be given in Ref.(8). In MC [5] one finds that there are two main decays, β and α -relaxation, separated by an intermediate quasinonergodic regime and by a power law decay (von Schweidler regime). The first may be preceeded by a fast decay

(in times of the order of the phonon times) and the last is followed by an ultimate decay to zero. A considerable amount of experimental evidence from neutron and light scattering experiments (see Ref.(5) for a review) lends support to this picture. This is clearly similar to the two-stage decay that we find at higher densities and smaller distances, with the two decays separated by a power law as explained below Equation (6). The phonon regime is absent in our data, probably due to the coarse graining nature of our Langevin dynamics. Comparison with MD is made difficult by the fact that existing results are for different systems, such as binary soft sphere mixtures [15] and coulombic systems [16], and that MD data is obtained under the questionable assumption that the equilibration time is of order t_k. However, a qualitative comparison is possible. For these purposes, we can take our phonon-based unit of time to be of order 0.1 ps. Refs.(15) and (16) cover then a time span comparable to ours, although they do not follow the correlations until they decay to a small value, as we do follow them. At any rate, after an initial glitch which they attribute to phonons, two distinct decays are observed in the MC data, the second of which is of a stretched exponential form. No characterization is given for the first, but we have verified that the form Eq.(6) fits quite well the data of Ref.(16) with appropriate parameter values (in particular, a large separation of the time scales). Thus, we conclude that our results are consistent with the predictions of MC and with MD results for similar systems.

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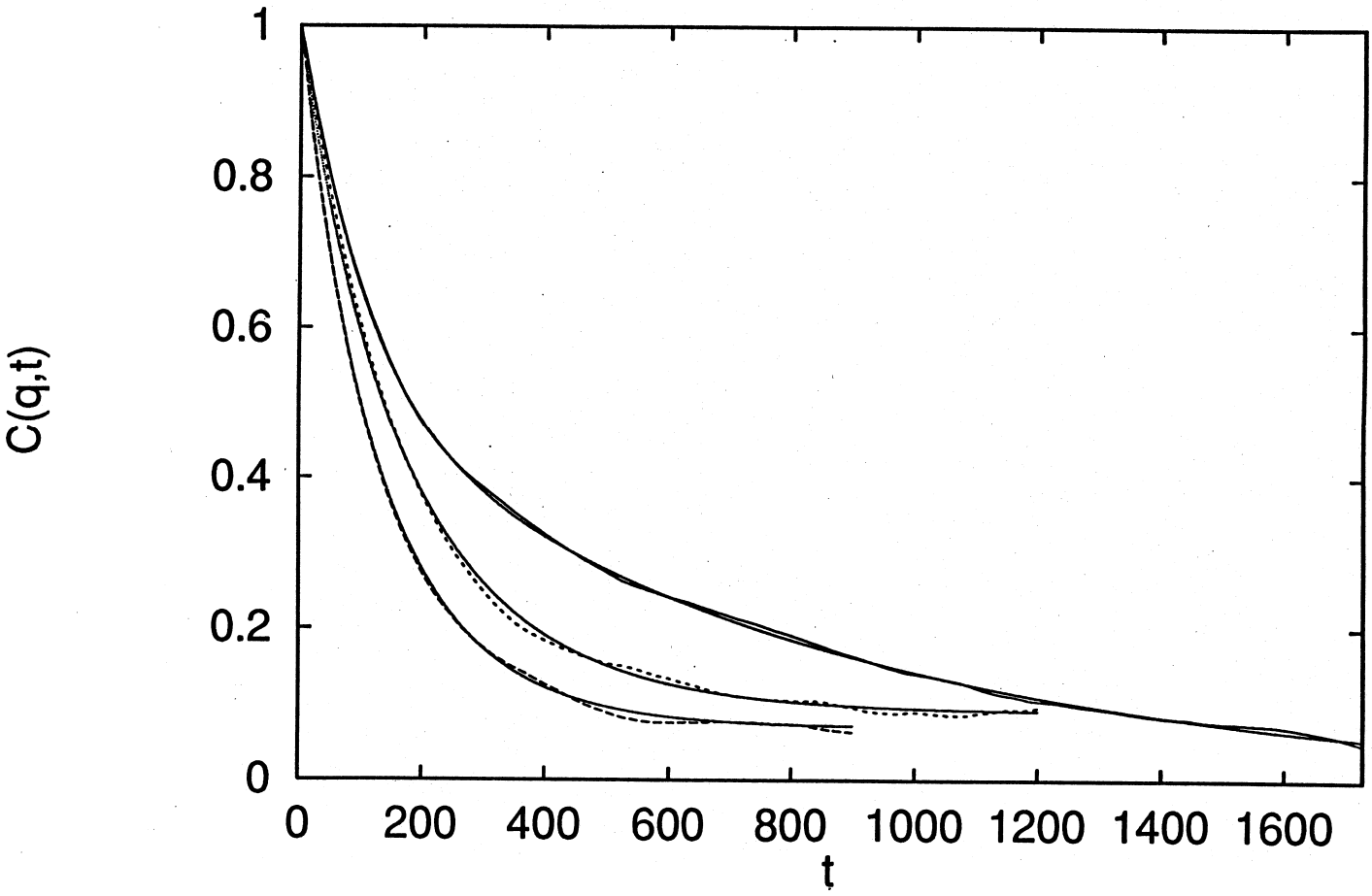
FIGURE CAPTIONS

Fig. 1. The normalized dynamic structure factor $C(q,t)$ as defined in the text, plotted vs time in dimensionless units. The plots are at constant density $n^* = 0.90$, and for wavevectors corresponding to, from top to bottom, $n_q = 13, 14, 12$. The dotted lines are our results, and the smooth solid lines fits to the form given by Eq.(6).

Fig. 2. As in Fig. 1, but for different densities at constant wavevector. The plots shown are for $n_q = 13$, and correspond to densities, from top to bottom, $n^* = 0.9, 0.85, 0.80, 0.75$. The fitting parameters at $n^* = 0.9$ are $f = 0.53$, $\tau = 107$, $\tau' = 761$.

Fig. 3. The characteristic slow time t^* as defined in the text, plotted as a function of density. The symbols are our results at the densities studied, and the solid line the fit to the Vogel-Fulcher law, as explained in the text.


C(q,t)
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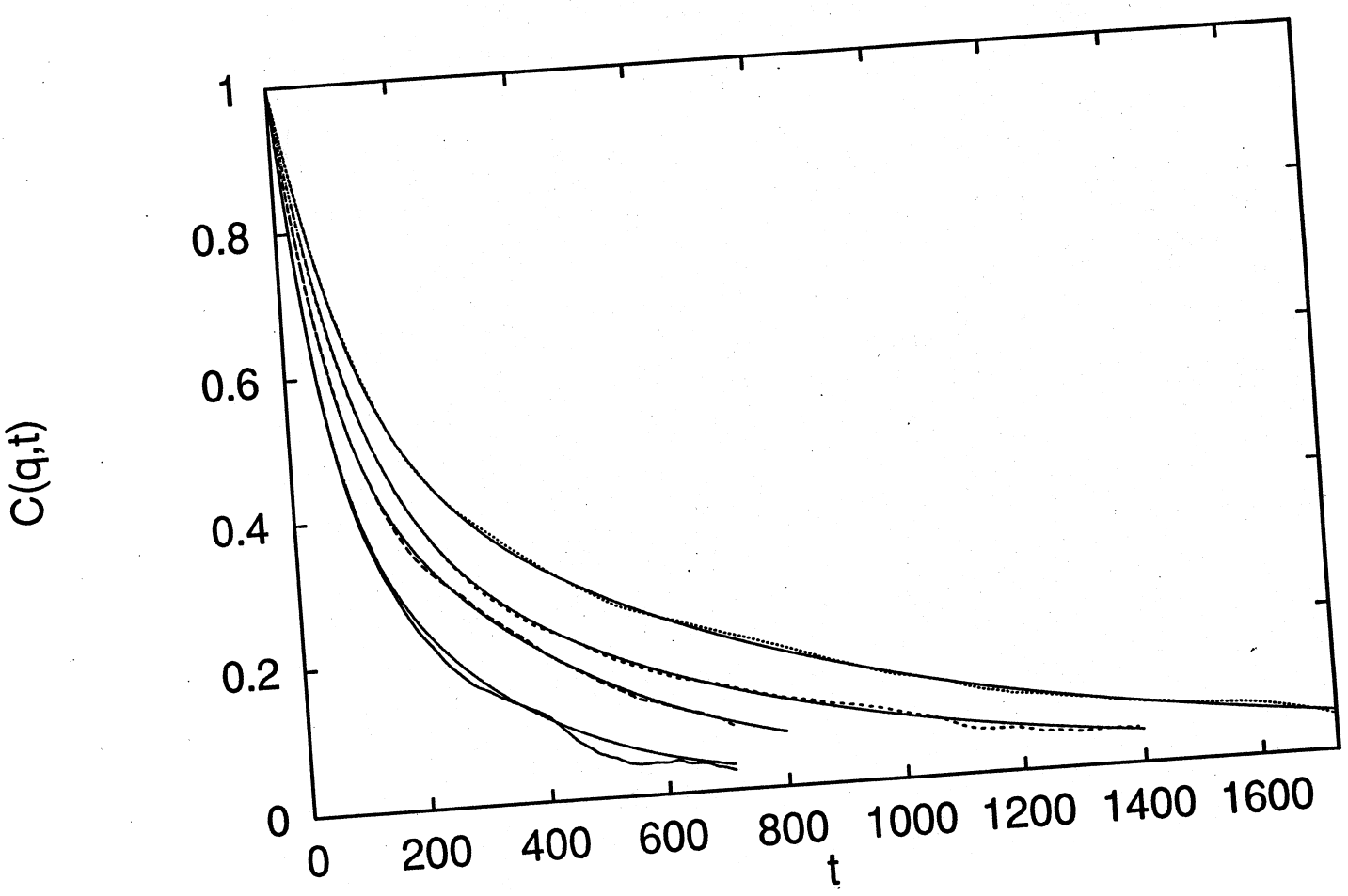
0.6
0.4
0.2
0
0
200
400
600
800
1000
1200
1400
1600
t


C(q,t)
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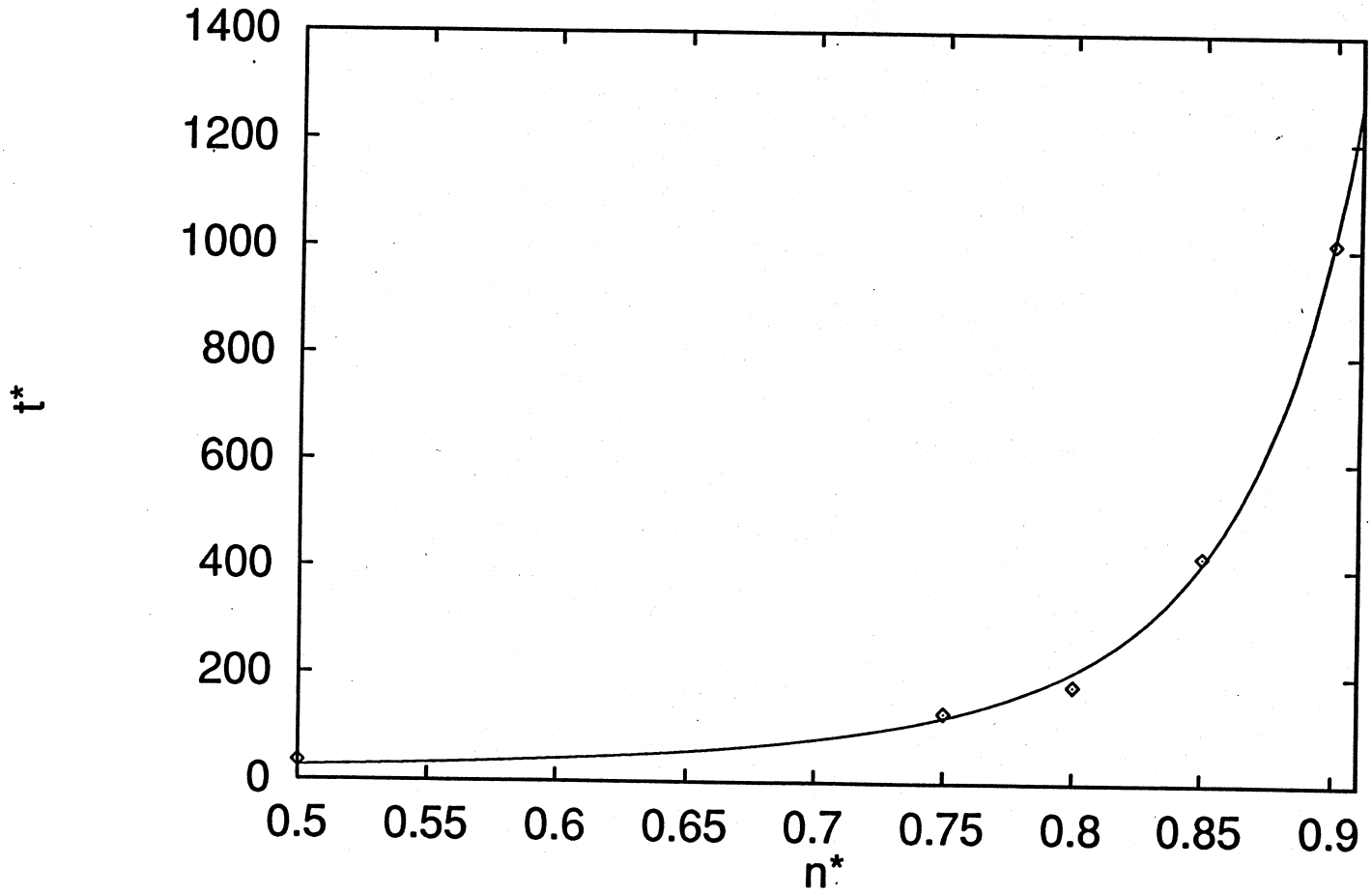
1400
1200
1000
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600
400
200
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t*
0.5
0.55
0.6
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0.85
0.9
n*